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PATENT TRADEMARK OFFICE

NASA Case No. 15851-1

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :
Kielin, Erik J., et al. :
Serial No.: 09/607,211 : Examiner: Nguyen, C.
Filed: June 30, 2000 : Art Unit: 1754
For: PROCESS FOR COATING SUBSTRATES WITH CATALYTIC MATERIALS

AFFIDAVIT UNDER 37 C.F.R. 1.131

I, David R. Schryer, being duly sworn, do hereby depose and say:

1. That I am one of the joint inventors of the claimed subject matter of the above identified U.S. patent application.
2. Prior to December 16, 1997, the joint inventors conceived and reduced to practice this claimed subject matter in the United States of America.
- ~~3. In support of my assertion that the claimed subject matter of the instant patent application was conceived and reduced to practice in the United States of America prior to December 16, 1997, I have attached, and made a part hereof, EXHIBIT A. EXHIBIT A is a photocopy of selected pages (pp. 19-22) from a NASA-LaRC Research Notebook. All critical dates in EXHIBIT A are prior to December 16, 1997.~~
4. The NASA Research Notebook excerpt, EXHIBIT A, gives details of a successful operational test of the subject invention claimed in the present application.

Further affiant sayeth not.

Attachment:
EXHIBIT A

David R. Schryer
David R. Schryer,

STATE OF VIRGINIA
CITY/COUNTY OF HAMPTON

Sworn to and subscribed before me by David R. Schryer, this 5th day of
September, 2002, in the aforesaid City and State.

Tim Z. Dwyer
Notary Public

My commission expires:
9/30/03



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4/3/96-SERIES:**EFFECT OF DILUTE NITRIC ACID ETCHING AFTER SnO_2 DEPOSITION ON THE SURFACE AREA AND FINAL ACTIVITY OF Pt/ SnO_2 CATALYSTS****PURPOSE:**

From the previously prepared and tested samples it is clear that etching in dilute HNO_3 (1.5-1.6 M) has a dramatic effect on both the surface area of the SnO_2 -coated, UNETCHED Cordierite and on the CO oxidation activity (> 400% conversion rate). Consequently one wants to know how etch time relates to SnO_2 surface area. Once this is known, it may finally be possible to determine the extent to which the Pt can be dispersed. If the activity levels off at some surface area of SnO_2 . It would be apparent that the Pt cannot be dispersed any further via this method of Pt coating.

EXPERIMENTAL:

The SnO_2 coating follows the same methodology as with the previously prepared samples (6/2/96-series) with the exception that 75% SnEH in acetone was used in the first deaeration and then a 2 parts SnEH -1 part acetone solution was used for the subsequent. The reason for changing the concentration from 50-50 was to decrease the time required to achieve the desired SnO_2 loading. Since it has been demonstrated that the SnEH concentration has little effect on the activity of the final catalyst, the concentration change does not present another variable here. A control, an unetched SnO_2 -coated sample, is being prepared with this series of samples which will take that variable into account anyway.

Data for the SnO_2 and Pt loadings is presented in the following tables as entitled.

 SnO_2 coating data-samples 1-4

Sample	1	2	3	4
W_{1i} , g	12.4152	12.6750	12.8140	12.3309
W_{1f} , g	13.7395	14.0066	14.1260	13.7205
ΔW_1 , g	1.3243	1.3316	1.3120	1.3896
W_{2f} , g	14.8642	15.0392	15.2017	14.7394
ΔW_2 , g	1.1247	1.0326	1.0757	1.0189
W_{3f} , g	15.8280	16.0220	16.2227	15.7102
ΔW_3 , g	0.9638	0.9828	1.0210	0.9708
W_{4f} , g	16.6552	16.8588	17.0790	16.5509
ΔW_4 , g	0.8272	0.8368	0.8563	0.8407
W_{oxide} , g	4.2400	4.1838	4.2650	4.2200
% oxide	25.458	24.817	24.972	25.497
\dagger g SnO_2/in^3	2.696	2.661	2.712	2.684

\dagger The volume of each piece is 37 by 34 cells or $37 \cdot 34 \cdot (0.5 \text{ in}) \cdot (0.05 \text{ in})^2 = 1.5725 \text{ in}^3$

26 March 96 *EDK*

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SnO₂ coating data-samples 5-8

Sample	5	6	7	8
W _{1i} , g	12.6651	12.5186	12.4760	12.6174
W _{1f} , g	14.0430	13.8353	13.8343	13.9497
ΔW ₁ , g	1.3779	1.3167	1.3583	1.3323
W _{2f} , g	15.2779	15.0456	15.1758	15.2090
ΔW ₂ , g	1.2349	1.2103	1.3415	1.2593
W _{3f} , g	16.2422	15.9190	16.0987	16.1413
ΔW ₃ , g	0.9643	0.8734	0.9229	0.9323
W _{4f} , g	17.1108	16.7232	16.9018	16.9039
ΔW ₄ , g	0.8686	0.8042	0.8031	0.7626
W _{oxide} , g	4.4457	4.2046	4.4258	4.2865
% oxide	25.982	25.142	26.185	25.358
†g SnO ₂ /in ³	2.827	2.674	2.814	2.726

†The volume of each piece is 37 by 34 cells or $37 \cdot 34 \cdot (0.5 \text{ in}) \cdot (0.05 \text{ in})^2 = 1.5725 \text{ in}^3$

ETCHING DATA

Sample No.	Etch time, hour	W _i , g	W _f , g	ΔW, g	% W loss	BET S.A. m ² /g
1	0	16.6552	16.6420	0.0132	0.0792545	21.6
2	5.25	16.8588	16.6774	0.1814	1.0759959	
3	4	17.0790	16.9364	0.1426	0.8349435	
4	9.5	16.5509	16.0087	0.5422	3.2759548	
5	17.2	17.1108	16.7764	0.3344	1.9543212	
6	24	16.7232	16.1640	0.5592	3.3438576	
7	38.5	16.9018	16.0847	0.8171	4.8343963	
8	47.5	16.9039	15.8870	1.0169	6.0157715	

The 1.6 M HNO₃ was changed every twenty-four hours for samples 6, 7, and 8.

It is possible that a temperature gradient existed in the beaker which may have affected the actual amount of material etched away. Consequently, there is not a clean linear relationship between etch time and % W loss. Furthermore, the temperature was apparently well below boiling as a greater percentage weight loss would have been expected than was achieved. The 6/2/96 samples, for instance, lost about 9% of their original weight in just a fraction of the etching time.

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PORE VOLUME DATA

Sample No.	1	2	3	4	5	6	7	8
Wi, g	18.7307	18.8553	19.1487	18.9361	19.4123	18.2222	18.8604	18.9994
Wf, g	16.6420	16.6774	16.9364	16.0087	16.7764	16.1640	16.0847	15.8870
ΔW , g	2.0887	2.1779	2.2123	2.9274	2.6359	2.0582	2.7757	3.1124
mL/g	0.12551	0.13059	0.13062	0.18286	0.15712	0.12733	0.17257	0.19591
34by34	15.3190	15.3254	15.6319	14.7215	15.4545	14.8788	14.8291	14.6427

It is unknown exactly how much SnO_2 or Cordierite is removed from the catalyst during the etching step. As a result, the Pt loading desired will be determined on a per unit bulk volume of Cordierite. In this way, the best use of Pt can still be determined from the CO oxidation activity. The Pt/ SnO_2 loading will be a minimum for the unetched sample (sample 1) by comparison to the others because no SnO_2 was removed. A PtAH solution concentration will be determined from this sample so as to give a 1% Pt/ SnO_2 loading. Dilutions to this solution will be made to gain the correct concentration for the other samples based on their water uptake.

Pt COATING AND FINAL CATALYST DATA-SAMPLES 1-4

Sample	1-0	2-5.25	3-4	4-9.5
mL H_2O /g	0.12551	0.13059	0.13062	0.18286
$\dagger W_{\text{SnO}_2}$, g	3.8999	3.8033	3.9036	3.7535
W_{Pt} req'd	0.03939	0.03842	0.03943	0.03791
W_{PtAH} req'd	0.06863	0.06693	0.06869	0.06605
$\dagger[\text{PtAH}]$ req'd	0.03569	0.03344	0.03364	0.02454
W_i , g	15.3190	15.3254	15.6319	14.7215
$W_{f_{\text{sol'n}}}$, g	17.2874	17.5934	17.5800	16.6403
$\Delta W_1 = \text{Vol sol'n}$	1.9684	2.2680	1.9481	1.9188
W_{PtAH} , g	0.06693	0.07711	0.06624	0.04797
W_{Pt} , g	0.03896	0.04489	0.03856	0.02792
% Pt/oxides	0.989	1.166	0.978	0.738
*g Pt/in ³	0.0270	0.0311	0.0267	0.0193
*g catalyst/in ³	3.38	3.44	3.38	3.11

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Pt COATING AND FINAL CATALYST DATA-SAMPLES 5-8

Sample	5-17.2	6-24	7-38.5	8-47.5
mL H ₂ O/g	0.15712	0.12733	0.17257	0.19591
†W _{SnO₂} , g	3.9344	3.6925	3.7031	3.7334
W _{Pt} req'd	0.03974	0.03730	0.03741	0.03771
W _{PtAH} req'd	0.06827	0.06407	0.06426	0.06479
[PtAH] req'd	0.02812	0.03382	0.02511	0.02258
W _i , g	15.4545	14.8788	14.8291	14.6427
W _{f sol'n} , g	17.3997	16.8440	16.9918	16.8308
ΔW ₁ =Vol sol'n	1.9452	1.9652	2.1627	2.1881
‡W _{PtAH} , g	0.04863	0.06682	0.05407	0.05470
W _{Pt} , g	0.02831	0.03889	0.03147	0.03184
% Pt/oxides	0.714	1.042	0.843	0.846
*g Pt/in ³	0.0196	0.0269	0.0218	0.0220
*g catalyst/in ³	3.22	3.28	3.15	3.17

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†This is only an estimate of the SnO₂ loading based on the assumption that equal amounts of Cordierite and SnO₂ are lost during etching. This will affect the numbers in g catalyst/in³ row.

*Volume of samples is 34 by 34 cells 34•34•(0.5 in)•(0.05 in)² = 1.445 in³; some sample was removed from each monolith after the oxide coating to perform BET surface area analyses.

‡The concentration of PtAH used for deaerating samples 1, 2, 3, and 6 was 0.034 g PtAH/mL and that used for samples 4, 5, 7, and 8 was 0.025. This gives near 1% Pt/SnO₂ loading and, for all samples, a more constant weight Pt per unit volume (g Pt/in³).

26 March '96 *ED Kellin*

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